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(73) Proprietor: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ (GB)
(84) **GB**

(73) Proprietor: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam (NL)
(84) **BE CH DE FR IT LI NL SE AT**

(72) Inventor: **Pike, Barry Graham**
April Cottage Pipers Lane
Lower Heswall Wirral Merseyside (GB)

(74) Representative: **Tonge, Robert James et al**
UNILEVER PLC Patents Division P.O. Box 68
Unilever House
London EC4P 4BQ (GB)

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Description

The invention relates to compositions for dyeing keratinous fibres, and more particularly to hair colourants.

For almost a century, p-phenylenediamine and p-toluylenediamine have both been recognized as primary intermediates in the dyeing of the hair. When mixed with hydrogen peroxide and applied to the hair, a proportion of the mixture migrates into the hair shaft and there reacts to form a permanent colour. However, this procedure suffers from three disadvantages: firstly, the need to keep the intermediate and oxidising agent separate until immediately prior to use, secondly, the need to mix the intermediate and oxidising agent properly immediately prior to use and, thirdly, the risk that excess oxidising agent might cause damage to the hair if too little intermediate is employed, or if mixing of intermediate and oxidising agent is incomplete.

Certain substituted p-phenylenediamines, notably 2-methoxy-p-phenylenediamine, also known as 2,5-diaminoanisole or 2,5-diaminomethoxybenzene, have been shown, for example in British Patent Specification No. 1 012 793, to be useful as dye intermediates in the dyeing of hair or wool, particularly in the presence of hydrogen peroxide, when a grey colour was obtained.

Certain other substituted benzene compounds such as 2,4-diaminophenol have also been known for many years as dye intermediates in the dyeing of hair by the formation of a permanent colour within the hair shaft after reaction with atmospheric oxygen. This principle is well established and is discussed, for example in Venkataraman K, (1971), "The Chemistry of Synthetic Dyes", Volume 5 at page 475 at seq., and particularly on page 497, where it is reported that a red-brown colour was obtained with 2,4-diaminophenol.

2-methoxy-p-phenylenediamine and 2,4-diaminophenol as their salts of mixtures thereof have also been proposed for use in the dyeing of hair. For example, CH—A—445 722 describes a hair cream containing *inter alia* 0.1% by weight of 2,5-diaminomethoxybenzene sulphate and 0.1% by weight of 2,4-diaminophenol hydrochloride. Also, FR—A—1 337 012 describes the dyeing of hair with freshly prepared aqueous solutions of either 2,4-diaminophenol dihydrochloride or 2,5-diaminoanisole dihydrochloride, each mixed with one other dye intermediate (but not with each other). Also, FR—A—1 372 525 describes the colouring of white hair with a highly alkaline aqueous solution containing 2,4-diaminophenol dihydrochloride and 2-methoxy-1,4-phenylenediamine sulphate, together with another hair dye precursor, to obtain a blonde colour.

In contrast with the aforementioned references, DE—A—1 492 256 states that a rich black colour is said to be obtained when white hair is treated with a dye solution containing no less than four dye precursors, namely, 2,6-dimethyl-1,4-diaminobenzene dihydrochloride, 3,4-diaminophenol sulphate, 2,6-diaminophenol dihydrochloride and 2,4-diaminomethoxybenzene sulphate.

In spite of the considerable amount of research which has been conducted in this field, it has hitherto not been possible to provide a system containing only two dye precursors based on an autoxidation reaction which will impart to living human hair, within a short contact time, a black or nearly black colour.

We have now, however, discovered that a mixture of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol can successfully be employed as dye precursors to impart a black colour to the hair, in the absence of a peroxide commonly used as an oxidising agent in the dyeing of hair.

Furthermore, we have shown that the addition of either p-phenylenediamine or p-toluylenediamine to a mixture of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol does not further enhance the dyeing operation nor do they influence the intenseness of the black color obtained.

Accordingly, the invention provides a container containing a peroxide-free dye composition including the dye procursors 2-methoxy-p-phenylenediamine and 2,4-diaminophenol or their respective water-soluble salts, characterised in that the dye precursors are the sole dye precursors, each precursor forming 0.5% to 10% by weight of the composition, the molar ratio of one dye precursor to the other being from 1:10 to 10:1, the composition having a pH value of from 7 to 10, and the container being closed so as to prevent the ingress of atmospheric oxygen sufficient to cause the dye precursors to oxidise prematurely.

It should be explained that "keratinous fibers" are fibres having the basis of the protein keratin. Although animal hair such as wool is an example of "keratinous fibres" and can accordingly be dyed using compositions of the invention, the invention herein is described and illustrated for convenience in terms of human hair which is a further example of "keratinous fibres". The invention is furthermore applicable both to "keratinous fibres", such as hair on the human head, and to wigs and hair pieces made from human hair.

The concentration of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, or their respective water-soluble salts, hereinafter referred to as "the dye precursors", in the composition is at lesat 0.5% by weight for each precursor. Preferably, each precursor forms from 1 to 8% by weight of the composition.

The minimum concentration of each dye precursor to be employed will also depend on the molar ratio of each, and on the total concentration of both dye precursors in the composition.

The molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol, or their respective water-solubl salts, in the composition is accordingly fr m 1:10 to 10:1, the preferred molar ratios being from 1:5 t 3:1, ideally 1:3 to 1:1.

If the dy precursors are employed at concentrations wh se m lar ratio is utside the range 1:10 to 10:1, it is unlikely that a g od black colour will be achieved.

The 2-methoxy-p-phenylenediamine is conveniently employed in the form of its sulphate-monohydrate weight: 254), as supplied for example by Aldrich Chemicals Limited. The 2,4-diaminophenol is conveniently employed in the form of its dihydrochloride salt (molecular weight: 197), as supplied for example by Koch Light Limited. When the pH of the composition is adjusted to a value from 7 to 10, these salts will give rise to the respective dye precursor bases.

The compositions according to the invention should be substantially free from oxygen in order to prevent oxidation of the dye precursors taking place before application to the hair. It is accordingly apparent that if either of the dye precursors is exposed to oxygen, then some oxidation is likely to occur, and the hair to which the composition is subsequently applied may not acquire a black colour. 2,4-diaminophenol is particularly prone to autoxidation in this way.

It is therefore necessary to ensure that all or substantially all oxygen is removed from the composition and that access of oxygen is prevented until such a time as the composition is required for dyeing hair.

The ingredients of the composition and the composition itself can be purged of oxygen by preparing and packing the composition in the presence of an inert gas such as for example nitrogen, carbon dioxide or a liquefiable gaseous propellant.

As an alternative, or additional to the use of an inert gas, the composition can contain an antioxidant to scavenge any oxygen that may come into contact with the dye precursors, either during manufacture of the composition or during storage prior to use.

When an antioxidant is employed, suitable antioxidants include, for example, ascorbic acid, sodium metabisulphite and sodium dithionite, or mixtures thereof, which should be employed in the composition in an amount sufficient to scavenge dissolved oxygen or gaseous oxygen enclosed within the headspace above the composition, while the composition is held in a closed container. Such antioxidants or mixtures thereof can usually be employed in the composition at a concentration of from 0.01 to 2%, preferably from 0.1 to 1% by weight of the composition.

It should be explained that where reliance is placed on the use as an antioxidant as an oxygen scavenger, compositions containing less than 0.01% by weight of antioxidant can contain oxygen that may not be fully scavenged by such a low level of antioxidant, whereas compositions containing more than 2% by weight of antioxidant can have their effectiveness diminished when applied to hair, due to interference with the autoxidation reaction on contact with atmospheric oxygen, on which the production of a black colour relies.

The compositions according to the invention can optionally also contain detergent, although care should be exercised in the choice and/or quantity of detergent employed, as some tend to reduce the intensity of the black colour of the dyed hair, or result in the development of colours other than black.

Suitable detergents for use in the process of the invention can be selected from anionic, non-ionic, amphoteric, zwitterionic and cationic detergents or mixtures of detergents from two or more of these classes detergents.

Examples of anionic detergents include alkyl benzene sulphonates, such as sodium alkyl benzene sulphonates and sodium alkyl naphthalene sulphonates; alkyl sulphates, particularly those having from 12 to 18 carbon atoms in molecule, such as sodium lauryl sulphate and triethanolamine sulphate; alkyl benzene polyoxyethylene sulphonates, particularly those wherein the alkyl radical has from 8 to 12 carbon atoms; sulphated monoglycerides, such as lauric monoglyceride sodium sulphate, lauric monoglyceride ammonium sulphate and sulphated cocomonoglyceride ammonium salt; alcohol ether sulphates; sarcosines, such as lauroyl sarcosine and cocoyl sarcosine; and sulphosuccinates, such as the dioctyl esters of the salts of sulphosuccinic acid.

Examples of cationic detergents include distearyl dimethyl ammonium chloride, dilauryl dimethyl ammonium chloride diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, cetyl trimethyl ammonium bromide, N-cetyl pyridinium bromide and benzethonium chloride.

Examples of amphoteric detergents include N-alkyl β-imino dipropionates, N-alkyl β-amino propionates and the basic quaternary ammonium compounds derived from 2-alkyl-substituted imidazoline such as hydroxyethyl carboxymethyl alkyl imidazolinium hydroxide (MIRANOL*), especially the lauric, myristic or stearic derivatives.

Examples of nonionic detergents include condensates of ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol (PLURONICS*); nonyl phenoxypoly(ethyleneoxy)ethanol (IGEPAL*), and polyoxyethylene(20) sorbitan monooleate (TWEEN* 80).

Suitable detergents for use in the process of the invention can also comprise soaps which are water-soluble salts of higher fatty acids and include alkali metal soaps such as sodium, potassium, ammonium and alkanol ammonium salts of straight chain saturated or unsaturated fatty acids containing from 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms. Preferred soaps include potassium, monoethanolamine, diethanolamine and triethanolamine soaps of C_{12} to C_{14} fatty acids, particularly of coconut fatty acids.

It has however been shown that when a detergent is to be incorporated into compositions of the invention, the pref rred anionic detergent is one chosen from Sodium lauryl ther sulphate (2EO), (such as EMPICOL* ESB 3S), and Sodium lauryl ether sulphate (3EO), (such as GENAPOL* ZRO), or a mixture thereof.

When a nonionic detergent is employed, it is preferably mixed with an anionic detergent in order to

increase foam volume when the composition is applied to the hair, without reducing the intensity of the black colour produced. Examples of pr ferred nonionic detergents are polyoxyethylene lauryl alcohol (23EO) (such as BRIJ* 35) and oleic diethanolamide, (such as MARLAMIDE* D 1885), or a mixture thereof.

The preferred detergent mixtur comprises sodium lauryl ether sulphate (2EO) with either of the above-named noni nic detergents.

The quantity of detergent when employed in the composition, will depend on which detergent is chosen and whether a mixture of detergents is employed. Whereas the use of a detergent assists application of the composition to the hair, in that a foam is produced which enables the user more readily to distribute the composition evenly onto and thoroughly into the hair, care must be exercised to ensure that the quantity of detergent employed is not so excessive that a black colour is not retained by the hair.

It is but a simple task to establish a suitable quantity of a detergent for this purpose by experimental application of a series of compositions containing differing amounts of detergent to switches of blond hair, and then selecting that composition which produces a pleasing black colour.

However, by way of example with reference to the preferred anionic and nonionic detergents referred to hereinbefore, the quantity of detergent that can be employed in compositions according to the invention is from 1 to 15%, preferably from 5 to 10% by weight of the composition, expressed in terms of active detergent.

If less than 1% by weight of any of the preferred anionic or nonionic detergents is employed, then it is unlikely that the consumer, when applying the composition to the hair, will obtain a significant lather from which the advantages of employing a detergent in the composition can be derived. If more than 15% by weight of any of the preferred anionic or nonionic detergents is employed, then application of the composition to the hair may yield an excessive volume of foam and may result in the development of a hair colour which is not a true black.

Ideally, the composition should contain a mixture of the preferred anionic and nonionic detergents at an active detergent ratio of 1:3.

The composition according to the invention can also optionally contain a thickening agent to enable it to be more easily dispensed from a container in a controlled manner, and more readily applied to the hair without, for example, running off the scalp.

Suitable thickening agents include: carboxyvinyl polymers such as CARBOPOL* 940 and CARBOPOL 941, and polyethylenglycol distearate or mixtures thereof.

Thickening agents such as these can be employed at a concentration of from 0.1 to 2%, depending on the choice of thickening agent. The Carbopols can, for example, be employed at a concentration of up to about 1% and the polyethyleneglycol derivative up to about 2% by weight.

It is also possible to include in compositions according to the invention other ingredients such as conditioners, polymers, preservatives and perfumes, and other ingredients such as are conventionally employed in products intended for the treatment of hair.

The invention also relates to a process for preparing a composition for use in the dyeing of keratinous fibres to produce a black colour, which process comprises the steps of:

(i) dissolving in oxygen-free water the dye precursors 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, the composition having a pH value of from 7 to 10; and
(ii) packaging the composition in a closed container in the substantial absence of oxygen.

The pH of the composition so prepared may be adjusted to the desired value of from 7 to 10, by addition of an alkali such as sodium hydroxide or ammonia, or by employing a suitable buffer.

According to a preferred process, the dye precursors are dissolved in an aqueous solution of an antioxidant so as to establish oxygen-free conditions, care being exercised to exclude oxygen, for example by purging with an inert gas.

Optionally, polar oganic solvents, such as isopropyl alcohol, may also be added to aid solution of the dye precursors.

The composition should be stored prior to use in a closed container from which it can be readily dispensed when required for application to the hair. The container or dispenser should preferably be one which is airtight or will at least prevent the ingress of atmospheric oxygen sufficient to cause the dye precursors to oxidise prematurely.

Suitable containers include plastic sachets, capped jars or tubes, pump spray operated applicators or pressurised aerosol devices in which liquefiable gaseous propellant can maintain a substantially oxygen-free headspace. The chosen design of the container, dispenser or applicator will depend partly on whether single or multiple dose application is intended, and partly on the means selected for ensuring that the composition is stored in a substantially oxygen-free state.

The preferred close container is designed to provide a single dose or so-called one pack product, the cont nts of which are sufficient to dye one head f hair.

The invention also provides a method for dyeing keratinous fibres which comprises applying to the keratin us fibres a composition comprising a substantially oxygen-free solution of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, and allowing these dye precursors to xidise in the presence f atmospheric oxygen.

When hair is to be dyed with compositions according to the invention, it is optionally first washed and then a proportion of the substantially oxygen-free solution containng the dye intermediates is applied to damp but not wet hair, to avoid over dilution of the dye precursors, and thoroughly rubbed in. By way of example, for a normal head of hair (about 70 g in weight) about 20 ml of an aqueous solution containing 0.4 M of both the dye precursors is applied to the damp hair. Both the duration and temperature of application to the hair will affect the final result obtained. In general, the longer the time and the higher the temperature of contact, the more intense is the black colour of ths dyed hair which finally results, but 10 to 30 minutes at room temperature (20° to 25°C) is usually sufficient for the development of a desirably intense black colour. Preferably, dyeing to a black colour is achieved without employing hydrogen peroxide as is conventional in a two-pack hair dye treatment.

It is also possible to apply repeatedly a dilute solution of the mixture of dye precursors in order to darken light or grey hair gradually until a desirably dark or black colour is obtained. As an example, an aqueous substantially oxygen-free solution of 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, each at a concentration of from 1 to 2% by weight can be applied to grey hair once or twice a day for about one week in order to obtain gradual darkening until a near black is obtained. Usually, 7 to 8 successive applications are sufficient to develop a good black colour to the hair.

Compositions according to the invention are particularly of value in the dyeing of human hair either attached to the head or in the form of a wig, hairpiece or switch. The compositions can however also be employed in the dyeing or natural keratinous fibres such as wool or silk or of synthetic keratinous fibres.

The invention is illustrated by the following Examples of "one-pack" compositions according to the invention containing both 2-methoxy-p-phenylenediamine (MPPD) and 2,4-diaminophenol (DAP).

Example 1

In this example a solution of both dye intermediates in the form of their respective salts was prepared in buffer and the solution stored under nitrogen to provide oxygen-free conditions.

Preparation of buffer

Sodium dihydrogen orthophosphate, 13.6 g was dissolved in water, 500 ml, and isopropyl alcohol, 150 ml, was added and the solution made up to 1 litre after adjustment of the pH with sodium hydroxide to 8.0.

Preparation of solution of dye intermediates

76.2 g MPPD (as the sulphate monohydrate salt) together with 19.7 g DAP (as the dihydrochloride salt) were dissolved in 1 litre of the buffer containing antioxidant to provide a concentration of 0.3 M with respect to the MPPD and 0.1 M with respect to the DAP.

This mixed solution was prepared under nitrogen and stored in the absence of oxygen until required for use.

Dyeing of hair

A switch of Italian "Blue String" virgin blond hair (about 1 g) was thoroughly wetted with tap water, excess water removed by blotting with filter paper and immersed in the oxygen-free solution containing the dye precursors in a 5 cm dish open to the atmosphere.

The switch was turned and agitated frequently with a glass rod during dyeing. After immersion for 20 minutes in the dye solution, the hair switch was rinsed and dried.

The switch of hair had a black colour.

In control experiments in which first the MPPD was omitted, and then secondly the DAP was omitted, similar switches of blond hair were dyed dark brown and pale blue/black respectively.

Example 2

This example illustrates the inclusion of detergents in compositions according to the invention. The following formulation was prepared as a "one-pack" product.

	% w/w
Ingredients	
Sodium lauryl ether sulphate (2EO) (EMPICOL ESB 3S:25% AD)	10.0
Thickener	
Carboxyvinyl polymer (CARBOPOL 940)	1.0
Dye intermediates	
2-methoxy-p-phenylenediamine:sulphate monohydrate salt (MPPD)	7.62
2,4-diaminophenol:dihydrochloride salt (DAP)	1.97
Solvent for MPPD	
Isopropanol	2.0
Antioxidant	
Sodium metabisulphite	0.5
pH adjustant to pH 8.5	
Ammonium solution	q.s.
Water	100

The concentration of MPPD can also be expressed as 0.3 M and that of DAP as 0.1 M.

The above "one pack" product was successfully stored for four months in the absence of oxygen, without deterioration or loss of viscosity, at temperatures ranging from 0°C to 50°C.

The product when applied to blond hair dyes it an intense black under the conditions described in Example 1.

Examples 3 and 4

Example 2 was repeated except that the CARBOPOL 940 thickener at a concentration of 1.0% by weight was replaced firstly with CARBOPOL 941 at a concentration of 0.9% by weight and secondly by polyethyleneglycol 6000 distearate at a concentration of 2.0% by weight.

Both of these modified one-pack products stored well without appreciable loss of viscosity under the conditions used in Example 2, and they both successfully dyed blond hair an intense black under similar conditions of use.

Examples 5 and 6

Example 2 was repeated except that sodium metabisulphite was replaced either with sodium dithionite (0.5% by weight) or with ascorbic acid (0.5% by weight).

In both cases, hair was dyed black under similar conditions of use.

Experiments

The following experiments illustrate the importance of the defined molar ratios of the dye precursors, the pH of the composition and the duration of contact with hair during the dyeing process.

Experiment A

The procedure described in Example 2 was also repeated except that the concentration of MPPD was 0.5% by weight (0.02 M), and that of DAP was 7.8% by weight (0.4 M). The molar ratio of MPPD to DAP in the composition was accordingly 1:20 which was also well outside the lower limit defined by the invention of 1:10.

Blond hair dyed using this composition was initially dark brown, but after a few days, the hair acquired a distinct redness.

Experiment B

The procedure described in Example 2 was repeated, except that the comp sition was adjusted to a pH valu f 5, which was b l w the l wer limit defined by the invention of 7.

Blond hair dyed with this composition acquir d a brown colour.

Experiment C

The procedure described in Example 2 was repeated, except that the composition was used to treat a switch of blond hair for only five minutes which was less than the minimum recommended time of 10 minutes.

The switch of hair acquired a brown col ur.

It was noted from these experiments that in each case a black colour was not obtained. This illustrates the importance of employing appropriate concentrations of dye precursors, pH of composition and duration of contact time as defined herein.

Claims

1. A container containing a peroxide-free dye composition including the dye precursors 2-methoxy-p-phenylenediamine and 2,4-diaminophenol, or their respective water-soluble salts, characterised in that the dye precursors are the sole dye precursors, each precursor forming 0.5% to 10% by weight of the composition, the molar ratio of one dye precursor to the other being from 1:10 to 10:1, the composition having a pH value of from 7 to 10, and the container being closed so as to prevent the ingress of atmospheric oxygen sufficient to cause the dye precursors to oxidise prematurely.

2. A closed container according to claim 1, in which the dye precursors of the dye composition each form from 1 to 8% by weight of the composition.

3. A closed container according to claim 1 or 2, in which the molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol, or their respective salts, in the dye composition is from 1:5 to 3:1.

4. A closed container according to claim 1, 2 or 3, in which the molar ratio of 2-methoxy-p-phenylenediamine to 2,4-diaminophenol, or their respective salts, in the dye composition is from 1:3 to 1:1.

5. A closed container according to any preceding claim, in which the solution is maintained in an oxygen-free condition by the presence of an antioxidant.

6. A closed container according to claim 5, in which the antioxidant is ascorbic acid, sodium metabisulphite or sodium dithionite.

7. A closed container according to claim 5 or 6, in which the antioxidant forms from 0.01 to 2% by weight of the composition.

8. A closed container according to any preceding claim, in which the dye composition additionally comprises a detergent.

9. A closed container according to claim 8, in which the detergent is an anionic detergent chosen from sodium lauryl ether sulphate (2EO) and sodium lauryl ether sulphate (3EO), or a mixture thereof.

10. A closed container according to claim 8, in which the detergent is chosen from polyoxyethylene lauryl alcohol (23EO) and oleic diethanolamide, or a mixture thereof.

11. A closed container according to any of claims 8 to 10, in which the detergent comprises a mixture of an anionic and a nonionic detergent.

12. A closed container according to any of claims 8 to 11, in which the detergent forms from 1 to 15% by weight of the composition.

13. A closed container according to any preceding claim, in which the composition additionally comprises a thickening agent.

14. A closed container according to claim 13, in which the thickening agent is chosen from carboxyvinyl polymers and polyethyleneglycol distearate, or mixtures thereof.

15. A closed container according to claim 14, in which the thickener forms from 0.1 to 2% by weight of the composition.

16. A closed container according to any preceding claim which is a plastic sachet.

17. A closed container according to any of claims 1 to 15 which is a capped jar or tube.

18. A closed container according to any of claims 1 to 15 which is a pump operated spray applicator.

19. A closed container according to any of claims 1 to 15 which is a pressurised aerosol device, in which liquefiable gaseous propellant can maintain a substantially oxygen-free headspace.

20. A process for the manufacture of a closed container containing a peroxide-free dye composition according to any preceding claim which process comprises the steps of:

- (i) dissolving in oxygen-free water 2-methoxy-p-phenylene diamine and 2,4-diaminophenol, or their respective salts, as the sole dye precursors, the composition having a pH of from 7 to 10; and
- (ii) packaging the composition in a closed container in the substantial absence of oxygen in such a manner as to prevent the ingress of atmospheric oxygen sufficient to cause the dye precursors to oxidise prematurely.

21. A method of dyeing keratinous fibres a black colour, which comprises applying to keratinous fibres in the absence of hydrogen peroxide, a composition dispensed from a closed container according to any of claims 1 to 19.

Patentansprüche

1. Behälter enthaltend eine peroxidfreie Farbstoffzusammensetzung, die die Farbstoff-Vorläuf r

2-Methoxy-p-phenylendiamin und 2,4-Diaminophenol oder deren jeweilige wasserlösliche Salze einschließt, dadurch gek nnzeichnet, daß die Farbstoff-Vorläufer die einzigen Farbstoff-Vorläufer sind, wobei jeder Vorläufer 0,5 bis 10 Gewichtsprozent der Zusammensetzung beträgt, das Molverhältnis von einem Farbstoff-Vorläufer zu dem anderen zwischen 1:10 und 10:1 beträgt, die Zusammensetzung einen pH-Wert zwischen 7 und 10 hat und der Behälter verschlossen ist, um das Eindrigen von Luftsauerstoff zu verhindern, der ausreicht, um eine frühzeitige Oxidation bei den Farbstoff-Vorläufern herbeizuführen.

2. Geschlossener Behälter nach Anspruch 1, dadurch gekennzeichnet, daß die Farbstoff-Vorläufer der Farbstoffzusammensetzung jeweils zwischen 1 und 8 Gewichtsprozent der Zusammensetzung ausmachen.

3. Geschlossener Behälter nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Molverhältnis von 2-Methoxy-p-phenylendiamin zu 2,4-Diaminophenol oder deren jeweiligen Salzen in der Farbstoffzusammensetzung in dem Bereich zwischen 1:5 und 3:1 liegt.

4. Geschlossener Behälter nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Molverhältnis von 2-Methoxy-p-phenylendiamin zu 2,4-Diaminophenol oder deren jeweiligen Salzen in der Farbstoffzusammensetzung im Bereich zwischen 1:3 und 1:1 liegt.

5. Geschlossener Behälter nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Lösung in einem sauerstofffreien Zustand in Anwesenheit eines Antioxidans gehalten wird.

6. Geschlossener Behälter nach Anspruch 5, dadurch gekennzeichnet, daß das Antioxidans Ascorbinsäure, Natriummetabisulfit oder Natriumdithionit ist.

7. Geschlossener Behälter nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß das Antioxidans zwischen 0.01 und 2 Gewichtsprozent der Zusämmensetzung ausmacht.

8. Geschlossener Behälter nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Farbstoffzusammensetzung zusätzlich ein Waschhilfsmittel enthält.

9. Geschlossener Behälter nach Anspruch 8, dadurch gekennzeichnet, daß das Waschhilfsmittel ein anionisches Waschhilfsmittel ausgewählt aus Natriumlaurylāthersulfat (2EO) und Natriumalurylāthersulfat (3EO) oder ein Gemisch davon ist.

10. Geschlossener Behälter nach Anspruch 8, dadurch gekennzeichnet, daß das Waschhilfsmittel aus Polyoxyäthylenlaurylalkohol (23EO) und Oleindiathanolamid oder aus einem Gemisch davon ausgewählt ist.

11. Geschlossener Behälter nach einem der Ansprüche 8 bis 10, dadurch gekennzeichnet, daß das Waschhilfsmittel ein Gemisch aus einem anionischen und einem nicht-ionischem Waschhilfsmittel enthält.

12. Geschlossener Behälter nach einem der Ansprüche 8 bis 11, dadurch gekennzeichnet, daß das Waschhilfesmittel zwischen 1 bis 15 Gewichtsprozent der Zusammensetzung ausmacht.

13. Geschlossener Behälter nach sinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Zusammensetzung zusätzlich ein Verdickungsmittel enthält.

14. Geschlossener Behälter nach Anspruch 13, dadurch gekennzeichnet, daß das Verdickungsmittel aus Carboxyvinylpolymeren und Polyäthylenglykoldistearat oder Gemischen davon ausgewählt ist.

15. Geschlossener Behälter nach Anspruch 14, dadurch gekennzeichnet, daß das Verdickungsmittel zwischen 0.1 und 2 Gewichtsprozent der Zusammensetzung ausmacht.

16. Geschlossener Behälter nach einem der vorhergehenden Ansprüche, welcher ein Kunststoffkissen ist.

17. Geschlossener Behälter nach einem der Ansprüche 1 bis 15, welcher ein mit einer Kappe versehenes Gefäß oder Tube ist.

18. Geschlossener Behälter nach einem der Ansprüche 1 bis 15, welcher ein Pumpsprühapplikator ist.

19. Geschlossener Behälter nach einem der Anspruche 1 bis 15, welcher eine Druck-Aerosol vorrichtung ist, bei dem ein verflussigbarer, gasförmiger Treibstoff einen im wesentlichen sauerstofffreien Luftraum halten kann.

20. Verfahren zur Herstellung eines geschlossenen Behälters mit einer peroxidfreien Farbstoffzusammensetzung gemäß einem der vorhergehenden Ansprüche, welches die folgenden Schritte umfaßt:

(i) Auflosen des 2-Methoxy-p-phenylendiamin und 2,4-Diaminophenol oder deren jeweiligen Salze in sauerstofffreiem Wasser als die einzigen Farbstoff-Vorläufer, wobei die Zusammensetzung einen pH-Wert zwischen 7 und 10 besitzt, und

(ii) Abpacken der Zusammensetzung in einen geschlossenen Behälter, wobei nahezu kein Sauerstoff gegenwärtig ist, um so das Eintreten von Luftsauerstoff zu verhindern, der ausreicht, um eine frühzeitige Oxidation bei den Farbstoff-Vorläufern hervorzurufen.

21. Verfahren zum Schwarzfärben von Keratinfasern, bei dem eine aus einem geschlossenen Behälter nach einem der Ansprüche 1 bis 19 abgegebene Zusammensetzung auf Keratinfasern in Abwesenheit von Wasserstoffperoxid aufgetragen wird.

Revendications

1. Récipient contenant une comp sition de teinture exempte de peroxyde contenant les précurseurs de teinture 2-méthoxy-p-phénylènediamin et 2,4-diamin phén l ou leurs sels respectifs solubles dans l'eau, caractérisé en ce que les pr curseurs de teinture sont les seuls précurseurs de teinture, chaque précurseur

formant de 0,5 à 10% en poids de la composition, le rapport molaire d'un précurseur de teinture à l'autre étant de 1:10 à 10:1, la composition ayant un pH entre 7 et 10, et le récipient étant fermé de manière à empêcher l'entrée de l'oxygène atmosphérique en une quantité suffisante pour provoquer l'oxydation prématuré . des précurseurs de teinture.

2. Récipient fermé selon la revendication 1, dans lequel les précurseurs de teinture de la composition de teinture représentent chacun de 1 à 8% du poids de la composition.

3. Récipient fermé selon la revendication 1 ou 2, dans lequel le rapport molaire de 2-méthoxy-p-phénylène-diamine au 2,4-diaminophénol ou leurs sels respectifs dans la composition de teinture est de 1:5 à 3:1.

4. Récipient fermé selon la revendication 1, 2 ou 3, dans lequel le rapport molaire de la 2-méthoxy-p-phénylène-diamine au 2,4-diaminophénol ou leurs sels respectifs dans la composition de teinture est de 1:3 à 1:1.

5. Récipient fermé selon l'une quelconque des revendications précédentes, dans lequel la solution est maintenue dans un état exempt d'oxygène par la présence d'un antioxydant.

6. Récipient fermé selon la revendication 5, dans lequel l'antioxydant est l'acide ascorbique, le métabisulfite de sodium ou le dithionite de sodium.

7. Récipient fermé selon la revendication 5 ou 6, dans lequel l'antioxydant constitue de 0,01 à 2% en poids de la composition.

8. Récipient fermé selon l'une quelconque des revendications précédentes, dans lequel la composition de teinture contient également un détergent.

9. Récipient formé selon la revendication 8, dans lequel le détergent est un détergent anionique choisi parmi le lauryléther-sulfate de sodium (2OE) et le lauryléther-sulfate de sodium (3OE) ou un mélange de ceux-ci.

10. Récipient fermé selon la revendication 8, dans lequel le détergent est choisi parmi le polyoxyoxyéthylène-lauryl-alcool (23OE) et le diéthanolamide oléique ou un mélange de ceux-ci.

11. Récipient fermé selon l'une quelconque des revendications 8 à 10, dans lequel le détergent comprend un mélange d'un détergent anionique et d'un détergent non ionique.

12. Récipient fermé selon l'une quelconque des revendications 8 à 11, dans lequel le détergent forme de 1 à 115% en poids de la composition.

13. Récipient fermé selon l'une quelconque des revendications précédentes, dans lequel la composition comprend en outre un agent épaississeur.

14. Récipient fermé selon la revendication 13, dans lequel l'agent épaississeur est choisi parmi les polymères carboxyvinyliques et le distéarate de polyéthylène-glycol ou leurs mélanges.

15. Récipient fermé selon la revendication 14, dans lequel l'épaississeur représente 0,1 à 2% en poids de la composition.

16. Récipient fermé selon l'une quelconque des revendications précédentes, qui est un sachet en matière plastique.

17. Récipient fermé selon l'une quelconque des revendications 1 à 15, qui est un bocal ou tube capsulé.

18. Récipient fermé selon l'une quelconque des revendications 1 à 15, qui est un applicateur par pulvérisation actionné par une pompe.

19. Récipient fermé selon l'une quelconque des revendications 1 à 15, qui est un dispositif d'aérosol sous pression dans lequel un propulseur gazeux liquéfiable peut maintenir un espace supérieur sensiblement exempt d'oxygène.

20. Procédé de fabrication d'un récipient fermé contenant une composition de teinture exempte de peroxyde selon l'une quelconque des revendications précédentes, procédé qui consiste:

(i) à dissoudre dans de l'eau exempte d'oxygène la 2-méthoxy-p-phénylène-diamine et le 2,4-diaminophénol ou leurs sels respectifs, comme seuls précurseurs de teinture, la composition ayant un pH de 7 à 10; et

(ii) à conditionner la composition dans un récipient fermé en l'absence pratique d'oxygène de manière à empêcher l'entrée de l'oxygène atmosphérique en une quantité suffisante pour provoquer une oxydation prématurée des précurseurs de teinture.

21. Procédé de teinture des fibres kératiniques en une couleur noire, qui consiste à appliquer aux fibres kératiniques en l'absence de peroxyde d'hydrogène une composition distribuée à partir d'un récipient fermé selon l'une quelconque des revendications 1 à 19.